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► **To cite this version:**

E. Hondros. SÉGRÉGATIONS INTERGRANULAIRES.GRAIN BOUNDARY SEGREGATION THE CURRENT SITUATION AND FUTURE REQUIREMENTS. Journal de Physique Colloques, 1975, 36 (C4), pp.C4-117-C4-135. 10.1051/jphyscol:1975413 . jpa-00216318

HAL Id: jpa-00216318

<https://hal.science/jpa-00216318>

Submitted on 4 Feb 2008

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SÉGRÉGATIONS INTERGRANULAIRES.

GRAIN BOUNDARY SEGREGATION THE CURRENT SITUATION AND FUTURE REQUIREMENTS

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Résumé. — Comme point de départ de cette revue, on propose que le phénomène de ségrégation aux joints intergranulaires peut être traité, en général, par les méthodes et les principes classiques de la chimie des surfaces.

On présente les principaux résultats expérimentaux et théoriques connus à ce jour, sur ce sujet :

- l'origine et la nature de l'activité intergranulaire,
- les isothermes d'adsorption qui y sont associés,
- la manière dont sont distribués les atomes ségrégués,
- les interactions entre les différentes espèces aux joints et l'anisotropie de la ségrégation.

Les études et les données nécessaires pour améliorer la connaissance de ce phénomène sont indiquées.

Abstract. — The point of departure of this review is that the phenomenon of grain boundary segregation in polycrystalline materials can be treated by the classical procedures and notions of surface chemistry. The main established experimental and theoretical features of reversible grain boundary segregation are assessed, together with a critical selection of the most important or most promising techniques for its study. This includes a discussion of the origin and nature of grain boundary activity, the various adsorption isotherms that are relevant, the form and distribution of grain boundary segregants, solute interactions at grain boundaries and the anisotropy of segregation. The deficiencies in our current understanding of the phenomenon are noted.

1. Introduction — segregation and surface chemistry. — The earliest interest in grain boundary segregation arose through a number of metallurgical observations on the mechanical behaviour of low alloy steels following various heat treatments. Such steels (in earlier times usually associated with the armaments industries), occasionally suffered a serious reduction in ductility, and the associated brittle failure revealed a high proportion of intergranular regions on the fracture surfaces. Later studies, based on ductile/brittle transition behaviour, showed that the phenomenon is time and temperature dependent, typically in the manner shown in figure 1. This demonstrates graphically

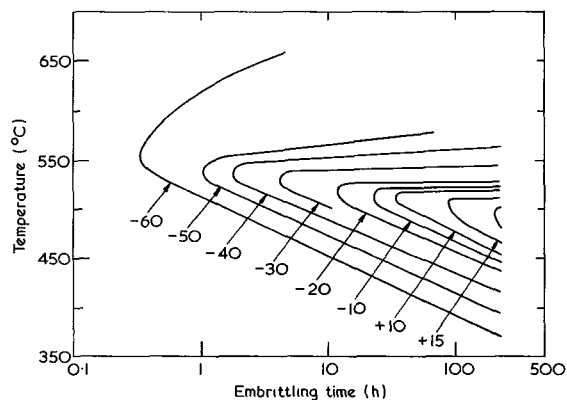


FIG. 1. — Typical isothermal embrittlement diagram, here in SAE 3140 steel: the resulting intergranular fracture is closely connected with segregation (Ref. [1]).

that optimum embrittlement occurs at about 550 °C, and if this particular steel is kept at this temperature for sufficient time, the ductile/brittle transition temperature may alter from -60 °C to +30 °C [1]. Lower temperatures of isothermal heat treatment require much longer times to produce a particular level of embrittlement. The diagram also demonstrates an important feature of the phenomenon of temper brittleness, its reversibility — the embrittlement can be removed by simply heating to temperatures above 650 °C and the non-embrittled state may be preserved by quenching from such high temperatures.

Several other important deductions were made through these earlier metallurgical observations, for example, susceptibility to temper brittleness requires the presence of certain residual impurity elements (such as phosphorus and antimony) in close association with alloying elements such as chromium and nickel, the impurity embrittling species being always within the solid solubility limits (see for example the review by Woodfine [2]).

A careful analysis of the large number of observations on mechanical properties led to the view that the source of this embrittlement is not the condensation of second phase precipitates at grain boundaries, as might be supposed, but rather the micro-segregation of impurity species at the grain boundaries by a thermodynamic equilibrium enrich-

ment process. Subsequently, considerable efforts were made to try to detect and measure this microsegregation. Because of the atomic dimensions of the phenomenon, it is not surprising that the techniques used were not adequate.

The emergence of suitable measurement techniques in recent years has permitted a closer study of the phenomenon, and, as will be enlarged on later, there is little doubt that the micro-segregation which leads to such dramatic effects on mechanical properties is a reversible interfacial segregation process, as was earlier envisaged by pioneers in this field such as McLean [3]. It should be mentioned at this point that there is evidence for the existence of a kinetics-dependent segregation at grain boundaries which is quite separate from the present phenomenon. It appears that the most ubiquitous form of grain boundary segregation is the equilibrium type, and in this review, the segregation discussed is taken to refer to the equilibrium phenomenon.

Because of its historical background, the subject of grain boundary segregation has been pursued largely by workers engrossed in its metallurgical consequences. As a result, it has evolved scientifically in a separate way from the discipline with which it is closely connected, namely, surface chemistry, in which a very large effort has been independently made and which has led to great technological advances, in for example, detergency. The position taken by this reviewer is that grain boundary segregation should be viewed as an aspect of surface chemistry and that the scientific methodology of surface chemistry and many concepts and rules developed in this long standing subject can be transferred with benefit and without loss of rigour to grain boundary segregation. Thus, for example, the notion of surface activity, so useful in surface chemistry, and which is a measure of an element's tendency to adsorb onto a free surface and reduce its energy, has its counterpart in grain boundary segregation, the term commonly used being Interfacial Activity.

A visualisation of grain boundary segregation in the context of surface chemistry is shown schematically in figure 2. A polycrystalline mass is held in an isothermal enclosure and at equilibrium the chemical potential of a surface active secondary species is the same in the vapour and in the solid phases. At equilibrium, there is a heterogeneous distribution of the surface active species, which concentrate at a free surface, grain boundaries, precipitate-matrix interfaces and other structural inhomogeneities such as dislocations. That this view is essentially correct is demonstrated for example by an experimental study of segregation of nitrogen at surfaces and grain boundaries in iron at high temperature using the technique of measuring changes in the surface and grain boundary free

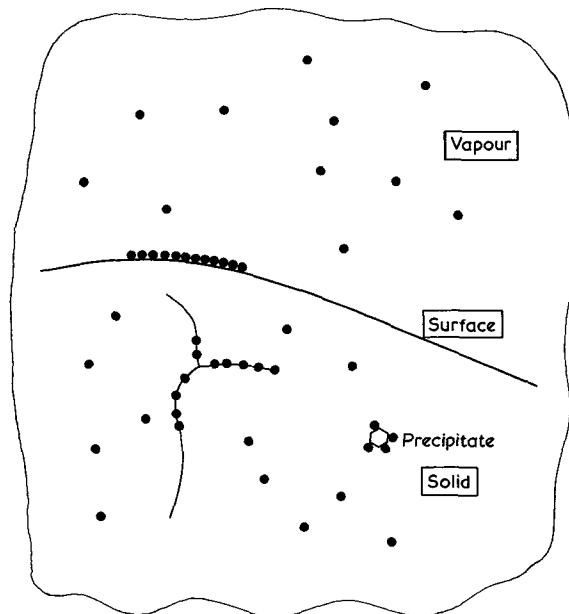


Fig. 2 — Schematic representation of chemical equilibrium in an alloy leading to adsorption at various interfaces.

energies [4]. The amount of nitrogen adsorbed to these interfaces was deduced by reference to either the bulk nitrogen solubility or to the partial pressure of nitrogen in the vapour phase, connected by the standard expression $[N\%] = K\sqrt{pN_2}$.

Within the framework of a surface chemistry approach, in this review, we shall consider in perspective the phenomenon of grain boundary segregation principally in terms of the experimental information that has come to light in recent times. A scientific understanding and a technological mastery of the phenomenon of grain boundary segregation with view to its deliberate control for the improvement of materials properties, requires information on a wide range of features, as follows :

- (i) The principal interfacially active species in a given system,
- (ii) The motivation for interfacial activity,
- (iii) The width of the grain boundary segregated layer,
- (iv) The dependence of segregation level on grain boundary type — segregation anisotropy,
- (v) The chemical state of segregating species — phase formation,
- (vi) Multiple segregation to grain boundaries — cooperative and competitive,
- (vii) The kinetic features of segregation,
- (viii) The nature of the sites for segregation within the grain boundary structure.

The subject has evolved very rapidly since the appearance of suitable techniques and we find that some of the above features can be answered satisfactorily now : one of the purposes of this review is to focus attention on those features which require further experimental and theoretical effort.

2. Detection and measurement of segregation. —

On referring to the copious literature on the detection and measurement of grain boundary segregation, one remarks at the wide range of often ingenious techniques deployed by research workers since the early 1930's to this end. In the light of new knowledge on the phenomenon, these earlier approaches are now seen to have been generally inadequate to provide unambiguous information, and some of these have but a passing historical interest. These can be classified as indirect techniques (including electrode potential measurements on fracture surfaces; various metallographic features at grain boundaries; kinetic effects such as grain growth; X-ray lattice parameter measurements; internal friction measurement; and, grain boundary energy measurements). There is also the category of direct technique (including the spectrographic analysis of material extracted from the grain boundary region; radio-tracer analysis; electron-probe micro-analysis and surface spectroscopy). The interested reader may refer to earlier accounts which deal in detail with these techniques, for example, Westbrook [5] and Inman and Tipler [6] and in a more recent review by Hondros [7]. Here we shall concern ourselves briefly with several important new technical developments for the detection and measurement of segregation, in the framework of the information requirements stated above.

The ideal technique for studying this phenomenon should have:

- (i) A high spatial and depth resolution, approaching the atomic scale,
- (ii) Be able to detect unambiguously any element,
- (iii) Be able to measure quantities present at a grain boundary,
- (iv) Provide information on the state of chemical binding of the segregant species at the grain boundary,
- (v) Be able to operate on non-exposed grain boundaries.

If one glances at the earlier techniques in relation to the above requirements, their inadequacies become obvious. The indirect procedures have a particularly serious disadvantage in that one requires an *a priori* knowledge of the surface active species. Thus, in applying such an indirect technique in a study of a multicomponent steel, one presupposes a knowledge of the surface active impurities — this knowledge arising from general metallurgical experience. In recent years, a range of sophisticated direct techniques have been developed for surface analysis, these being based on a variety of processes such as secondary electron emission, sputtered ion mass spectrometry, ion beam scattering, and field ion microscopy with the atom probe. These have been treated at various

levels of detail in a number of publications. It seems at the present stage that not one single technique can satisfy all the above requirements, but used in complementary capacities, most of the required information for grain boundary segregation studies can now in principle be derived. Here we consider briefly three techniques — (1) Auger Electron Spectroscopy (AES) which has already proved to be a powerful technique for segregation studies, (2) Field Ion Microscopy (FIM) and (3) Electron microscopy with energy analysis.

The success and general acceptance of *Auger Electron Spectroscopy* in recent years in connection with segregation studies is no doubt due to its sensitive detectability and high depth resolution, making it into a powerful surface chemical analysis technique. The analysis is usually carried out in an ultra high vacuum chamber immediately following the *in situ* fracture of the specimen. The exposed fracture surface is then free from contamination from the ambient atmosphere for some hours. The Auger emission process in essence requires the excitation of the surface by a primary electron beam in the range 1-3 keV, followed by the detection of characteristic Auger electrons that are emitted and which are manifested in sharp peaks in the derivative in the secondary electron energy spectrum. The usefulness of this process as a surface analysis technique lies in the fact that the Auger electrons which escape through the surface arrive typically from the first couple of atom layers. The physics of Auger electron emission in relation to its use as a spectroscopic technique has been treated in a number of recent publications (Gallon and Matthew [8]) and also the use of AES in connection with segregation studies has been described by a number of authors (for example, Seah and Hondros [9], Joshi and Stein [10]). Because the primary exciting beam can be focussed, spot sizes of the order of several microns can now be used for chemical analysis of metallurgical events on fracture surfaces, and a further advantage of the technique is that the probe can be scanned across the surface to provide an image of the fracture topography that is being investigated. A further recent refinement is that the instrument can be arranged to produce a scanning view of a particular Auger electron signal, thereby displaying the surface distribution of a species. An example of an Auger spectrum from a temper embrittled steel (5 NCMV) is shown in figure 3. This illustrates the fine chemical analysis detail, free from background noise, that can be obtained typically from a fracture surface.

The power of AES lies in this ability to detect unambiguously whatever surface active species lies on a grain boundary fracture surface, and in many cases, to provide a quantitative measure of the relative proportions. For certain practical metallur-

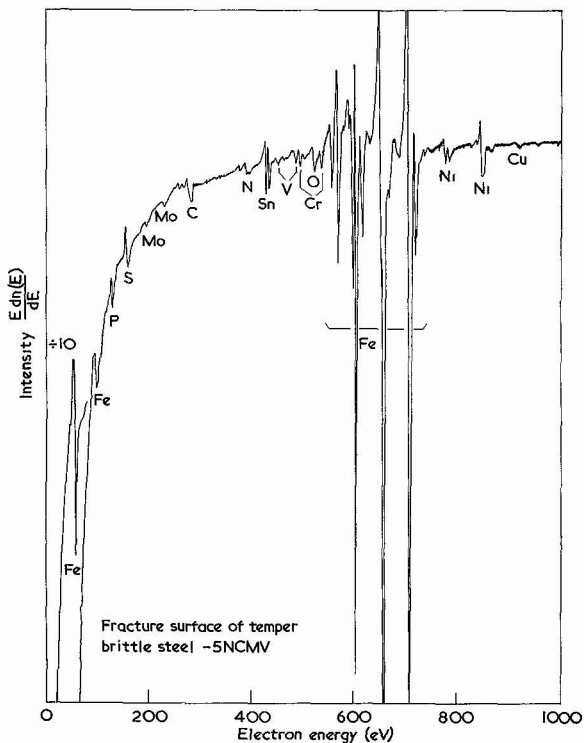


FIG. 3. — Auger electron spectrum obtained from the intergranular fracture surface of 5NCMV steel, showing with good resolution a number of co-segregating species.

gical situations, this capability is of primary importance and greatly outweighs its deficiencies. From the point of view of a detailed scientific description of the segregation phenomenon, one shortcoming of AES is the difficulty of quantifying the spectra from certain important systems, such as that of carbon in iron. Another, perhaps temporary disadvantage, is that chemical binding information cannot be obtained with ease, although recent advances have been made, based on fine spectral structure (Grant and Haas [11]) and also observations on plasmon loss peaks in the Auger spectrum (Seah [12]). Again, since the Auger electron signal is an integrated response from the area that is being irradiated, the technique cannot provide detailed structural information such as the association of solute atoms with particular sites or features at the grain boundary. An aspect that is generally overlooked and which may prove to be one of the most serious disadvantages of AES viz-à-viz segregation studies is the requirement for the exposure of the grain boundary surface by fracture. This limits the use of the techniques to systems in which there is strong segregation associated with reduced grain boundary cohesion. There are in fact metallurgical situations in which the segregation is at a level that may not reduce the grain boundary cohesion substantially but which may produce important secondary effects, for example, accelerated high temperature creep cavitation or grain boundary corrosion.

In order to circumvent the deficiencies in capability of the above technique in both practical and scientific situations, *Field Ion Microscopy* holds considerable promise. Here, as is well known, individual atoms on a surface can be imaged at a magnification of about 1 million times by ionisation of an inert gas at the surface in the presence of a high electric field. Such fields are of the order of 3 V per Å, which can be obtained in practice at a sharp specimen tip about 1 000 Å in diameter. The promise of «FIM» has in recent years greatly increased in relation to segregation studies since it was demonstrated that it can deliver chemical information through the time-of-flight mass spectrometer, or *atom probe*. Here, a selected atom on the surface is erased by field evaporation and passed into a mass spectrometer for identification. A recent example provided by Dr P. Turner [13] of Cambridge University is illustrated in figure 4, and

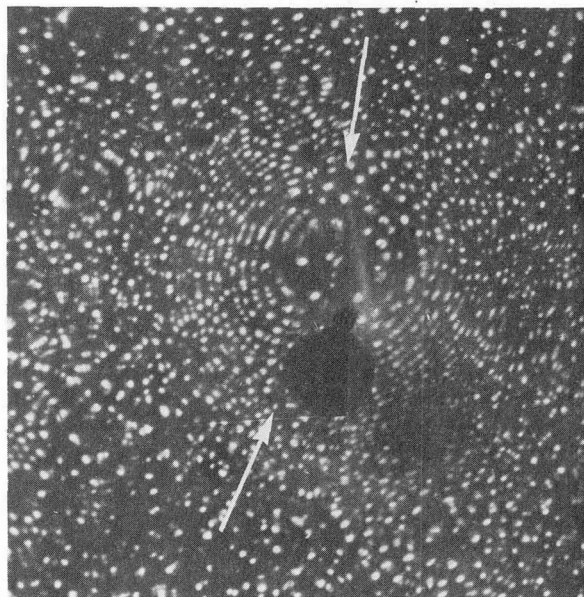


FIG. 4. — Field ion micrograph of a martensite lath boundary in an iron-carbon alloy: there is evidence of *bright spot* decoration in the boundary region (Dr. P. Turner, Cambridge).

this shows a martensite lath boundary in steel. The corresponding field evaporation spectrum from the boundary region is shown in figure 5, indicating that the boundary is associated with segregated carbon atoms which may be discerned as bright spots in the FIM micrograph. It is very likely that a technique such as this should be able to reveal the grain boundary sites associated with segregant atoms. The further use of the technique in analysing the precipitate constituents of steel (Brenner and Goodman [14] on nitrides in steel; Turner and Papazian [15] on Mo_2N and Mo_2C in steels) suggests that it can be extended reliably to the study of grain boundary embryo-phase formation during early stages of segregation.

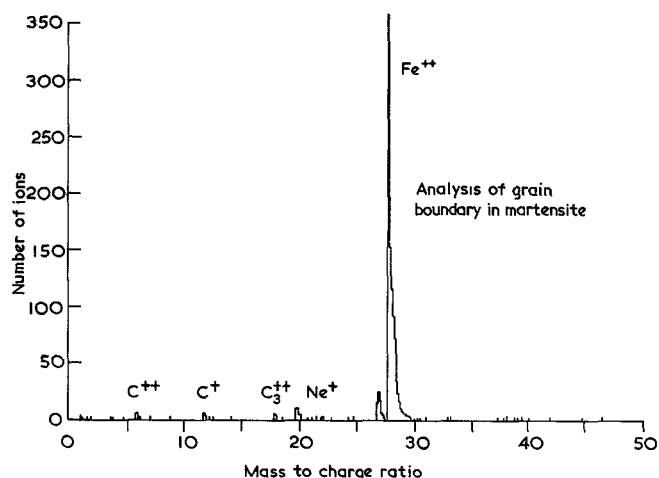


FIG. 5. — Atom probe analysis of the martensite lath boundary of figure 4 showing a 2 : 1 enrichment of carbon above the background count, and also the presence of carbon clusters (Dr. P. Turner, Cambridge).

One technical disadvantage of the above technique is that under the intense electrical field at the tip, a field which generates stresses close to the theoretical cohesion stress of the metal, there is a high probability of rupture of the segregant-weakened boundary. This appears to limit the technique in practice to systems which are not severely embrittled, or for low levels of segregation that do not produce a significant reduction in cohesion; in this respect, this technique is the exact converse of AES.

Transmission Electron Microscopy combined with Energy Analysis also holds promise as a technique for a full quantitative chemical analysis of segregation at integral grain boundaries. In recent years, a number of instruments have been developed which incorporate X-ray and electron spectrometers with conventional transmission electron microscopy and which allow the display at high magnification of an area which is them chemically analysed. In the energy analysis microscope, the analysis is obtained by measurement of the characteristic energy losses of transmitted electrons, these losses originating in inelastic scattering in the material, the amount of scattering depending on the nature of the species present. Thus in principle, segregation information can be obtained on a thin foil specimen which presents a grain boundary parallel to the direction of the incident beam. This was used successfully for the analysis of light elements by Cundy *et al.* [16] who constructed an instrument with energy resolution of 1 to 2 eV to be used for energy loss measurements in the range 0 to 15 eV. Because the analysis is based on the measurement of plasma losses, the technique is restricted to light metals such as the alloys of aluminium with magnesium, zinc and copper, and it has been extended to a number of metallurgical applications as described recently by Edington and

Hibbert [17]: for example, the measurement of concentration profiles during a precipitation process. A typical grain boundary concentration profile obtained by characteristic energy loss measurements is shown in figure 6, obtained by Doig and Edington [18] on an Al-7% Mg alloy on an instrument having a spatial resolution of about 100 Å. Quantitative analysis is normally obtained by calibrative procedures using alloys of known composition. In figure 6, a symmetrical grain boundary depletion about the grain boundary has been clearly measured — the composition far from the boundary is that of the bulk, while that at the grain boundary is much lower.

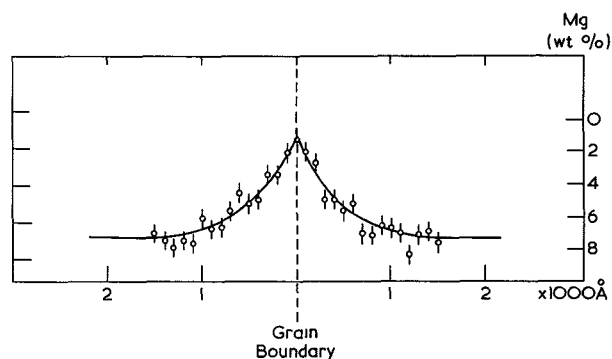


FIG. 6. — Demonstration of symmetrical grain boundary depletion of Mg in an Al-7% Mg alloy, by transmission Electron Microscopy in association with Energy Analysis (Ref. [18]).

Although the spatial resolution displayed in figure 6 is satisfactory for a number of metallurgical processes (for example, diffusion profiles, and probably also for the study of non-equilibrium segregation effects), for the study of equilibrium segregation, the resolution is obviously not sufficient and also its restricted use to light metals is another serious disadvantage. However, important recent advances associated with Crewe and his group have been made in Transmission Scanning Electron Microscopy in which a high brightness gun based on a field emission source is used (see Clarke [19] for a recent review). With such a source, a spot size of 3 Å is in principle attainable. This, combined with energy loss analysis makes it a very attractive possibility to study all processes associated with grain boundary enrichment. At the present time, work is in progress at the Cavendish Laboratory in Cambridge to detect and measure grain boundary segregation in copper-bismuth alloys that had previously been characterised using other techniques.

3. Gibbsian or equilibrium segregation. — Grain boundary segregation has been occasionally referred to as *Gibbsian* segregation to distinguish it from other types of segregation, which depend on the kinetics of solute transport to interfaces and which give rise to concentration profiles different

from the ones observed in equilibrium processes. How accurate is this description of *Gibbsian* segregation? Here it will be argued that grain boundary segregation can be correlated with changes in grain boundary free energy and that the segregation is a true Gibbsian adsorption.

A foundation of liquid phase surface chemistry is the Gibbs Adsorption Theorem, which relates a change in surface tension to the surface concentration, deriving either from solution or from the vapour phase. In its most general form, this is expressed by

$$d\gamma = -SdT - \sum \Gamma_i d\mu_i$$

where γ is the surface tension, S the surface entropy and Γ_i is defined as the *superficial density* of a component i which has a chemical potential of μ_i . In fact there have been a number of attempts to verify the theorem experimentally by direct measurement of the surface excess using tagged radioactive species, and fair agreement was obtained on binary inorganic solutions: see Adamson [20] for an interesting account of such experiments and also for his comments on the philosophical implications of a failure to find an agreement.

The application of this theorem to measure segregation at grain boundaries in earlier work [21] was to some extent through an act of faith, but supported by the internal consistency of the results. One of the reasons for a *lingering doubt* on the applicability of the theorem to internal interfaces is in the difference that lies between the nature of the surface between a condensed phase and a vapour phase, and the surface between two crystalline phases such as a grain boundary. In the case of a free surface, the standard Gibbs device of *mathematical dividing surface* chosen arbitrarily so as to make the surface concentration of the solvent Γ_1 to vanish, is a useful notion to describe a surface excess in a manner that is conveniently visualised. There are, however, conceptual difficulties in applying this convention to solid-solid interfaces such as a high angle grain boundary. Here, the concentration profiles of Γ_1 and Γ_2 should be approximately symmetrical across the interface, and it is not possible to assign a dividing surface to make either one vanish. Alternative conventions for describing the surface excess were considered by Guggenheim and Adam [22]. In one of these which we adopt here, the equilibrium excess at a grain boundary is defined as the excess of a solute component contained in a grain boundary segment of unit area above that contained in an identical volume of matter in the interior. The above authors proved that in a system in which the second component is very dilute and in which the thickness of the interface is vanishingly small, the present convention gives rise to the same results as in the Gibbs convention.

The system iron-tin was studied by Seah and Hondros [9] both by measuring the grain boundary energy as a function of bulk tin content, and also by measuring directly the tin segregation on grain boundary fracture surface using Auger Electron Spectroscopy. Thus a comparison could be made between the values of the grain boundary enrichment as deduced from the use of the Gibbs approach and by the direct approach. Figure 7 shows the variation of grain boundary energy of

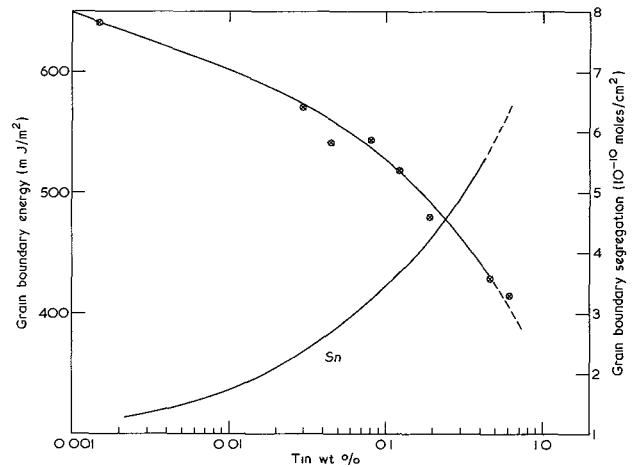


FIG. 7. — Dependence of grain boundary energy of iron on bulk tin content at 1420 °C and the derived grain boundary adsorption isotherm (Ref. [9]).

iron at 1420° C as a function of the bulk tin content, and superimposed on the figure are the values of Γ_{Sn}^b as derived from the form of the Gibbs equation appropriate to dilute conditions, namely,

$$\Gamma_{\text{Sn}}^b = -\frac{1}{RT} \left(\frac{\partial \gamma_b}{\partial \log_e X_{\text{Sn}}} \right)_T$$

and expressed here as moles of Sn per cm² of grain boundary surface. The value of the Gibbs enrichment of tin at the grain boundary for a bulk tin content of 0.25 per cent is also plotted in figure 8, together with values obtained on the same alloys by Auger spectroscopy appropriate to temperatures below 900 °C. Unfortunately it is not experimentally possible at this stage to apply both techniques on specimens at the same temperature: the grain boundary energy approach applies to high temperatures while the Auger Electron Spectroscopy for this system has to be conducted for heat treatments below the γ -phase transformation, as it would not be practicable to quench specimens from the bcc phase at 1420 °C. Figure 8 shows that within experimental scatter, the value of the grain boundary segregation obtained by the Gibbs approach falls on the extrapolated curve for the low temperature values. In both sets of experiments a large number of boundaries were sampled to obtain

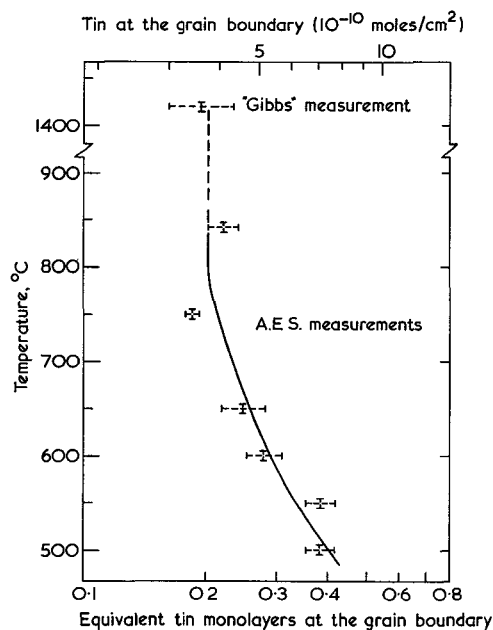


FIG. 8. — Segregation of tin to iron grain boundaries, as measured by the *Gibbs* adsorption approach and also directly by Auger Electron Spectroscopy (Ref. [9]).

each datum point and the experimental scatter is a reflection of variability between boundaries as well as measurement error.

This demonstrates a reasonably quantitative confirmation of the applicability of the adsorption theorem to segregation at grain boundaries and proves the validity of the concept of a Gibbsian segregation at average high angle grain boundaries. Further, perhaps circumstantial support for the applicability of the Gibbs Adsorption Theorem to grain boundaries can be seen in the results shown later in the diagram of figure 18, which includes values obtained both by Auger spectroscopy and by grain boundary energy measurements. The generalised treatment of the data over a large number of systems derived from several laboratories provides strong proof that the grain boundary segregation on average boundaries can be considered as a true Gibbsian segregation.

4. Distribution of segregants. — In the application of the Gibbs Adsorption Theorem for deducing interfacial excess, it was conveniently supposed that the solute segregation was spread out uniformly as a two-dimensional layer along the grain boundary plane. Since the thermodynamic approach measures the integrated effect of many solute atoms within the force field of the grain boundary and which may change the free energy of the boundary, this method cannot provide information on the localised distribution of segregants.

A full analysis of grain boundary segregation behaviour requires a knowledge of how the segregant species are distributed across the boundary, whether the segregation is spread uniformly in the

plane of the boundary, and thirdly, whether the amount of segregation varies significantly with grain boundary geometry. With the recent availability of suitable techniques that allow an examination of the grain boundary chemistry and the fine structure of the boundary at an atomic resolution, we are entering a period when the above information should be attainable.

4.1 SEGREGANT PROFILES ACROSS THE BOUNDARY. — One of the earliest contributions made by Auger Spectroscopy to segregation studies was to demonstrate beyond any reasonable doubt that segregation is constrained, in general, to a narrow locality close to the grain boundary plane. This is demonstrated clearly in figure 9 for some ferrous systems which display temper brittleness [23]. This represents a plot of the normalised Auger electron yield as a function of distance from the initial fracture surface. The curve shows half of a symmetrical concentration profile about the plane of the boundary. Similar results have been obtained in other laboratories for other systems — for example, in copper-bismuth [24] and in iron-sulphur and iron-tin [9]. The method used for erasing the surface in order to carry out the analysis is always by ion beam sputtering, which can lead to errors in that the sputter yield for each species from the alloy substrate is required in order to determine the depth of material removed. In general, such sputter yields are not known and the pure element sputter

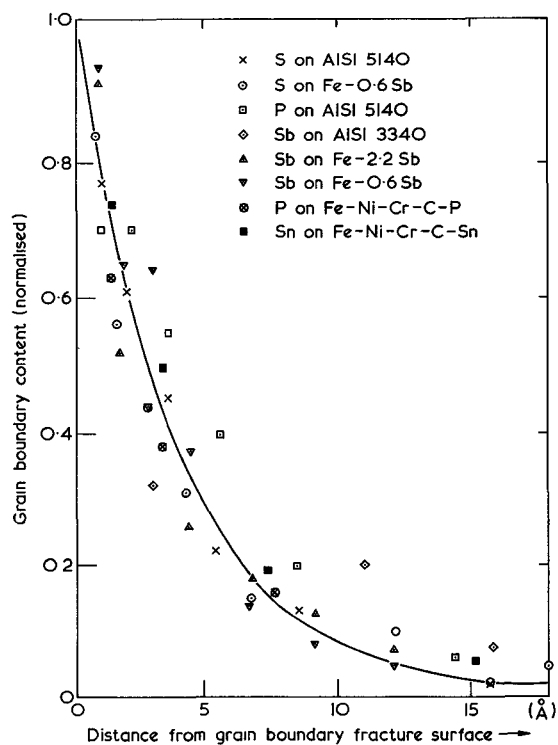


FIG. 9. — Profile of distribution of segregating species in a number of steels with distance from grain boundary fracture surface, illustrating the narrow width of segregation (Ref. [23]).

yield is assumed. In spite of this, Seah and Hondros [9] argued that for tin and sulphur on iron the respective sputter yields from this substrate should be less than that in the pure elemental state and consequently one can define an upper limit of the concentration profile extending approximately up to four layers of tin and three layers of sulphur on each side of the boundary, these values representing the tail of the profile where the concentration is significantly above that of the bulk.

By these procedures, there is wide agreement that surface active solutes segregate very close to the grain boundary, within the first one or two atom layers. The exception so far found is that of nickel in steels, for which both Marcus *et al.* [23] and Joshi and Stein [10] find independently that the nickel profile extends to much larger distances, as shown in figure 10. Here, from the work of the latter authors, the high nickel levels extend to beyond 100 atom layers.

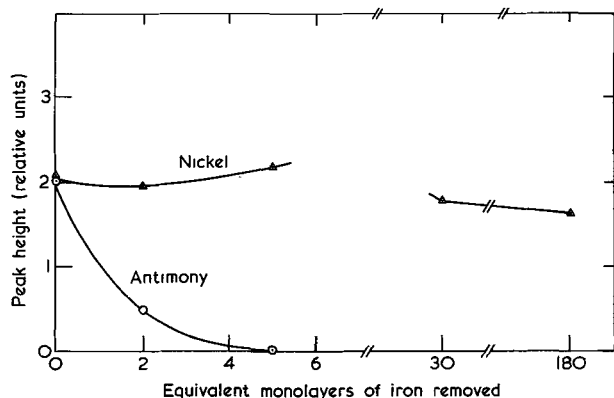


FIG. 10. — Grain boundary concentration profiles of Ni and Sb in iron, showing that Ni appears to persist at high levels to considerable distances into the interior (Ref. [10]).

4.2 FORM AND DISTRIBUTION OF SEGREGANT WITHIN THE PLANE OF THE BOUNDARY. — On a grain boundary model having a periodic structure, one might expect corresponding periodicities in the distribution of segregant within the same grain boundary plane — perhaps localised cluster formation, or short range order, appropriate to the formation of a two-dimensional phase of near intermetallic composition, in a manner similar to the formation of a two-dimensional surface phase, as demonstrated experimentally by Domange and Oudar [25].

The finest practical probe size of the Auger spectroscopy is of the order of a micron, and with this, measured variations in segregation coverages will not reflect the fine periodic structure of a grain boundary. In this respect, several workers have made and carefully repeated Auger spectroscopy measurements over a single grain boundary fracture surface and found that in general, variations in the

Auger electron signal lie within the experimental scatter of the technique and can usually be accounted for by factors such as specimen geometry (Seah [26]). In one detailed study, some results of which have been reproduced in figure 11, Powell [27] measured the Bi-Cu Auger electron peak ratios within and across many large grains in a sample of Cu-0.02% Bi. As can be seen, within any grain, the signal ratios are generally within 20%.

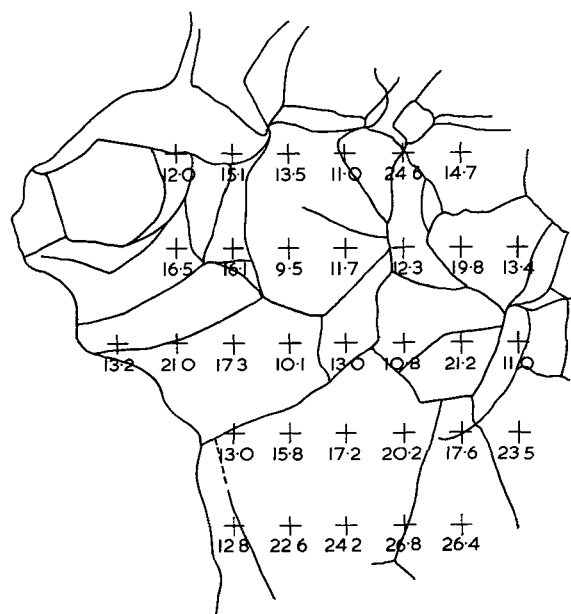


FIG. 11. — Map of a grain boundary fracture surface in a polycrystalline Cu-Bi alloy with the distribution of Bi/Cu Auger Electron peak ratios within and between grains (Ref. [27]).

It is to Field Ion Microscopy with its atomic resolution that one must turn to for information on the lateral distribution of solute atoms and its correlation with the grain boundary structure. There have not been many investigations of this nature. Smith and Smith [28] examined grain boundaries in oxygen-doped tungsten, and associating bright spots with oxygen atoms, deduced a very sharp grain boundary enrichment of oxygen above the bulk level. However, the form of the segregation profile did not reflect behaviour as shown above using Auger spectroscopy and there may be some doubt as to whether all the bright spots can be associated unequivocally with oxygen atoms. In another study of grain boundaries in recrystallised tungsten-chromium alloys, Howell *et al.* [29] detected segregated chromium using the technique of field evaporation which preferentially retains solute atoms which in turn appear as bright spots. As reproduced in figure 12, the chromium atoms which appear as black spots are distributed at random throughout the boundary plane and a systematic analysis of plots such as this did not indicate any periodic variations in the number of chromium atoms per unit area.

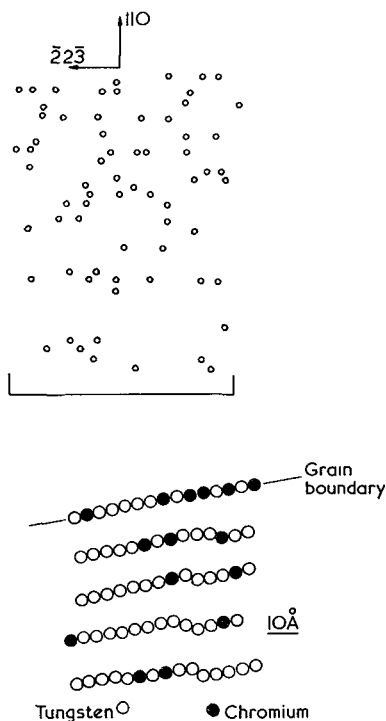


FIG. 12. — Field Ion Microscopy plot of the distribution of Cr atoms in a W-Cr alloy: upper diagram, in the plane of the boundary; lower diagram, successive positions of the grain boundary (Ref. [29]).

Although this type of study is at an early stage, it is promising, especially with the advent of atom-probe analysis in conjunction with FIM, so that identification of the solute atoms will be unequivocal and one more source of uncertainty will have been removed. Eventually, studies such as this should disclose how the solute is distributed laterally in a boundary in terms of the crystallographic parameters of the boundary. So far, only several grain boundaries have been investigated in this way, and short range order in the distribution of the segregant has not been revealed: perhaps only boundaries with special orientations will manifest a periodic distribution of segregant along the grain boundary plane.

4.3 SEGREGATION ANISOTROPY: DEPENDENCE ON GRAIN BOUNDARY TYPE. — In the same way that surface adsorption is known to be anisotropic (see for example, Hondros and McLean [30]), extending the general arguments of the introduction lead one to expect that the amount of segregation should depend on the nature and crystallography of the grain boundary. From a thermodynamic standpoint, considering a population of boundaries of variable energy γ_i in a closed system, and further assuming a uniform probability of occurrence of any type of boundary, a maximum reduction in total grain boundary free energy $\sum_i \eta_i \gamma_i$ will be achieved if the grain boundaries with higher free energies are

reduced proportionally more, i.e. if segregation should be more dense on the high angle boundaries. The observation by Howell *et al.* [29] by FIM that chromium does not segregate to the boundary of a coherent twin is generally consistent with the above view.

The system Fe-Sn-S studied by Auger electron fractography revealed a surprisingly low segregation anisotropy [9]. A typical set of histograms indicating the S/Fe and Sn/Fe Auger electron signal ratios from the fracture surfaces of an Fe-1% Sn-0.003% S alloy, is shown in figure 13. The histogram (1 of 35 similar sets of data for different compositions) derives from a random sample of 15 boundaries on the same fracture surface: both sets of results, typical of all the histograms, show a standard deviation from the mean of about 10%, a scatter which can well be accounted for by experimental factors such as fracture surface inclination to the analysing beam.

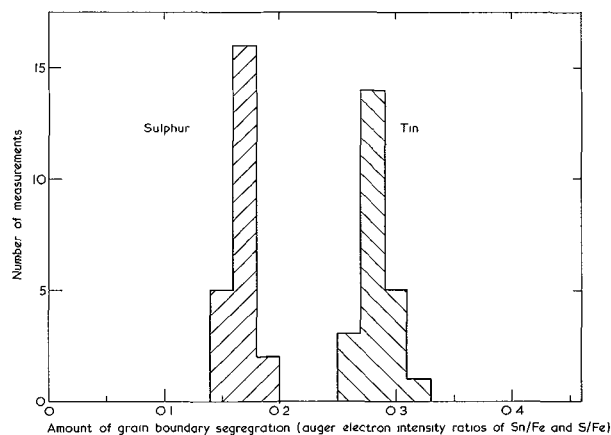


FIG. 13. — Histogram of distribution of S/Fe and Sn/Fe Auger Electron signal ratios from the fracture surface of an Fe-S-Sn alloy, showing the narrow width of distribution (Ref. [9]).

It should be noted, that in this type of study there is an aspect of the experimental technique which may distort the results. Thus figure 14 is a schematic drawing of a stressed polycrystal showing a

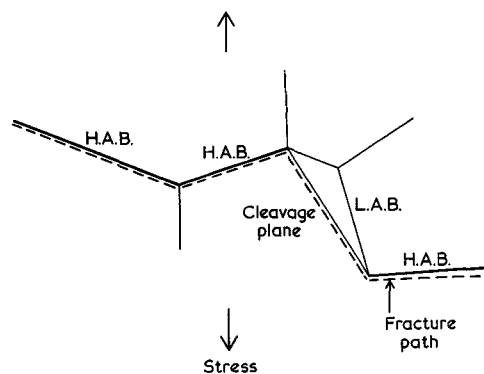


FIG. 14. — Schematic diagram showing how the fracture path may select grain boundaries of high segregation level and low cohesion.

grain boundary network of high angle and low angle grain boundaries. If the segregation is anisotropic, the high angle boundary having a greater solute concentration than the low angle boundaries, one would expect that the grain boundary cohesion would be reduced more for the former boundaries than for the latter. Depending on the orientation of the stress axis in relation to the boundary surfaces, fracture might follow a path as shown in the diagram, which, the geometry permitting, bypasses the low angle boundaries via a cleavage route. In such a case, the combination of cohesion and localised maximum resolved tensile stress for a cleavage plane favours the rupture of this plane rather than the nearest low angle boundary which has a slightly lower cohesion but also a lower resolved tensile stress. In this way, the fracture process may tend to select grain boundaries having a particularly low cohesion, that is, maximum segregation. This might help to account for the observations in (bcc) Fe-Sn-S alloy that there is little spread in Sn and S segregation among the many grain boundaries that were sampled.

In the case of the Cu-Bi investigation mentioned above, however, cleavage fracture cannot occur. Thus, Powell [27] observed marked variations in Bi/Cu ratios from boundary to boundary as shown in figure 11 in a sample of Cu-0.02% Bi having a large grain size and on which the surface was scanned at 0.25 mm intervals with the gun at normal incidence. On this segregation distribution map the grain boundary concentration of bismuth represented by the higher values of the Bi/Cu signal ratios corresponded to about 1 monatomic layer. A factor of 3 variation in Auger electron signal ratio from boundary to boundary is noted here. Although the Auger electron emission is anisotropic, the large acceptance angle of the energy analyser used in this work smooths out this effect. We note also that the fracture surface with low signal ratios (that is low bismuth concentration) showed a characteristic ductile tearing type of intergranular fracture in contrast with the high segregation areas which showed smooth intergranular decohesion. All these observations are consistent with the view that grain boundary segregation is highly anisotropic — thus, the low bismuth segregation is associated with a smaller reduction in cohesion and hence the fracture occurs in a semi-ductile manner.

The view then, that grain boundary segregation should depend significantly on grain boundary orientation has been confirmed in a semi-quantitative way in the alloy Cu-Bi. A more complete study requires a correlation between the amount of segregation and the crystallographic parameters defining the grain boundary. A fractographic approach, such as that by Auger spectroscopy, in which the grain boundaries are exposed for examination, may introduce artefacts and dis-

tort the results. Eventually, techniques such as FIM and Scanning Transmission Electron Microscopy on the unfractured grain boundaries should provide detailed information.

4.4 GRAIN BOUNDARY FACETING INDUCED BY SEGREGATION. — A corollary of high grain boundary segregation anisotropy is that where the geometry permits, a high angle grain boundary could decompose into a stepped structure composed of alternating segments of different characteristics, so that the average grain boundary energy per unit area of the newly formed structure is lower than that of the original structure. This has been a fairly well characterised phenomenon for free surfaces where it is generally agreed that it is promoted by the preferential adsorption of a vapour species onto certain planes. In some situations, it has been shown to be a reversible phenomenon, so that the motivation is clearly the reduction in surface free energies: in other situations, the surface morphology is controlled by the kinetics of evaporation. In the same way, a growing internal interface during the appearance of a new phase may show a corrugated structure, due to differences in the rate of growth of certain facets.

Segregation to grain boundaries may or may not favour facet formation, depending on the types of grain boundary segments that the original boundary breaks up into. Consider for example, an average high angle boundary in a pure single component system. It is energetically possible for this boundary to break up into alternating grain boundary segments of low energy — presumably semicoherent interfaces or structural segments with a good coincidence fit, as shown schematically in figure 15. The energy condition for facet formation is

$$A' \gamma'_b + A'' \gamma''_b < A \gamma_b$$

where A , A' , A'' are the areas of the respective segments of grain boundary. Recently, faceting of this type has been observed in pure zinc by Bishop *et al.* [32], one example of their work being

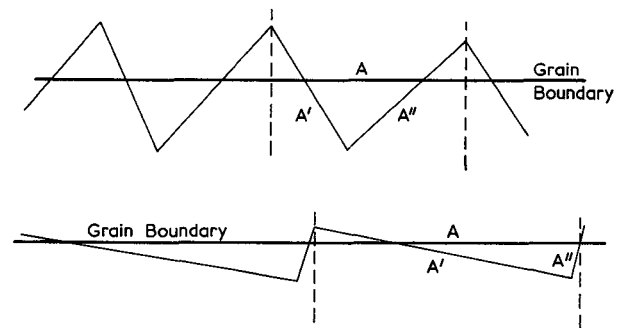


FIG. 15. — Schematic representation of possible types of grain boundary stepped structures.

reproduced in figure 16. Now in the presence of segregation, the energy of the original high angle boundary will be reduced much more than γ_b' or γ_b'' , assuming that these are boundary segments of good geometrical fit or high coincidence. Thus, in this case, segregation should favour the preservation of the initial high angle grain boundary and should not lead to faceting. In fact this was qualitatively confirmed by Bishop *et al.* [32] who observed that faceting of grain boundaries in zinc depended on the impurity level, and that samples from a part of the zinc ingot which was rich in impurities showed less incidence of facet formation.

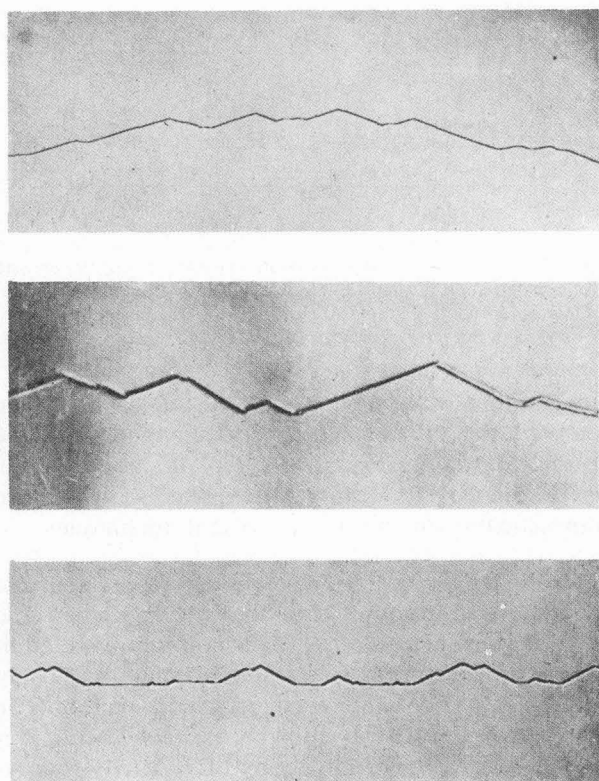


FIG. 16. — Micrographs of grain boundary faceting in pure Zn (Ref. [32]).

Various hypothetical situations can be envisaged: for example, a grain boundary having a structure or orientation not susceptible to segregation. If segregation is highly anisotropic, this initial boundary may break up into two segments of high segregation potency, or again into one highly coherent plane of no segregation and a small fragment with high segregation potency, as shown schematically in figure 15. Depending on the relative areas of the grain boundary fragments, the energy condition may be satisfied.

Thus from the above, since segregation reduces the boundary free energy, in general, it should tend to stabilise the boundary from the point of view of formation of a stepped structure. Although theoretic-

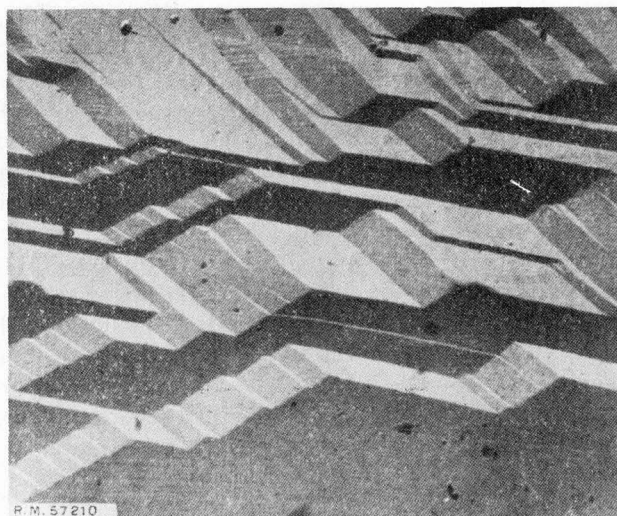


FIG. 17. — Appearance of fracture surface of a nickel alloy, showing highly faceted structure (Ref. [33]).

cally there are situations where segregation might induce a stepped structure, the geometrical and energetic constraints are so rigorous that one might not expect this to be a common phenomenon. Some years ago, Henry *et al.* [33] published a number of observations of facet formation on the fracture surfaces of nickel and interpreted these in terms of segregation promoted faceting. An example of this striking form of grain boundary faceting is shown in figure 17, which is very reminiscent of the features observed on thermally etched free surfaces. Since that date, very few observations of this type have been made. Recently Pichard *et al.* [34] noticed similar striation markings at grain boundaries in the vicinity of oxide inclusions in pure iron containing a small quantity of selenium. Since, in the numerous observations on grain boundary fracture surfaces, especially since the advent of scanning electron microscopy, this phenomenon has not been noted often, it probably confirms our judgement above that because of the strict energetic and crystallographic conditions required, segregation induced faceting is not a phenomenon of real importance. We note, that if this were a common phenomenon at a sub-microscopic scale, it would have important consequences on ideas of grain boundary cavity formation in creep conditions and also on the initiation of grain boundary fracture.

5. Interfacial activity. — Solute species possess varying tendencies to segregate to grain boundaries. This *interfacial activity* is the analogue of surface activity, employed frequently in surface chemistry studies. In the appreciation of segregation behaviour among various systems, this is a parameter of primary importance and already a good body of data has been accumulated.

In the earliest attempts to describe interfacial activities, before the advent of surface spectro-

scopy analysis, the quantity $(d\gamma_b/dX)_{x=0}$, that is, the slope of grain boundary energy versus bulk concentration (as illustrated in figure 7), at zero concentration, was adopted as a useful measure of the tendency to segregate. Such earlier results, based upon these measurements, are reproduced in figure 18, where the interfacial activity is plotted against the maximum solid solubility of the surface active species in the particular binary system [21]. This presentation of data was arrived at by purely empirical procedures: it was felt that the interfacial activity should be reflected in some physico-chemical parameter that measures the tendency for a solute to be rejected by the lattice, the most convenient of which is the inverse solid solubility.

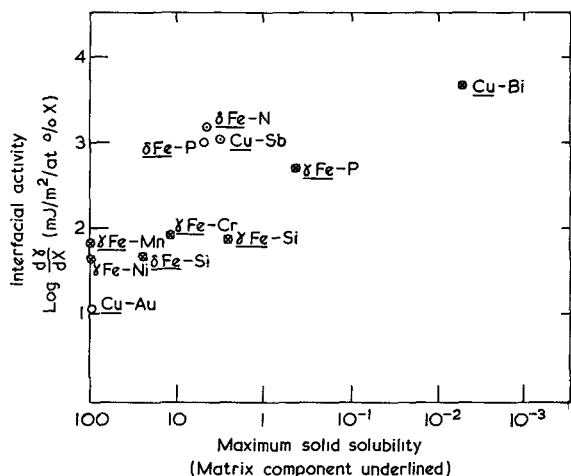


FIG. 18. — Interfacial activity in a number of binary systems plotted against the maximum solid solubility of the second component in the solvent (underlined) (Ref. [21]).

A new compilation of the experimental data available at the time of writing is shown in figure 19, which includes values obtained in several laboratories, using both the earlier grain boundary energy approach and also the surface spectroscopy approach. These two figures, 18 and 19, illustrate the rapid advances made in this subject in the last years and it especially reflects on the value of a technique such as Auger Electron Spectroscopy. Here, the interfacial activity is represented by the quantity β , the Enrichment Factor — the ratio between the grain boundary solute content and the bulk solute content. A further refinement which results in a greatly improved correlation is that the value of the solid solubility is that appropriate to the temperature of the measurement rather than the overall maximum solid solubility as in the former correlation. The least squares fit to the data are clearly expressed by

$$\beta \propto \frac{1}{X_0}$$

where X_0 is the solid solubility at the measurement temperature. From this diagram one may predict

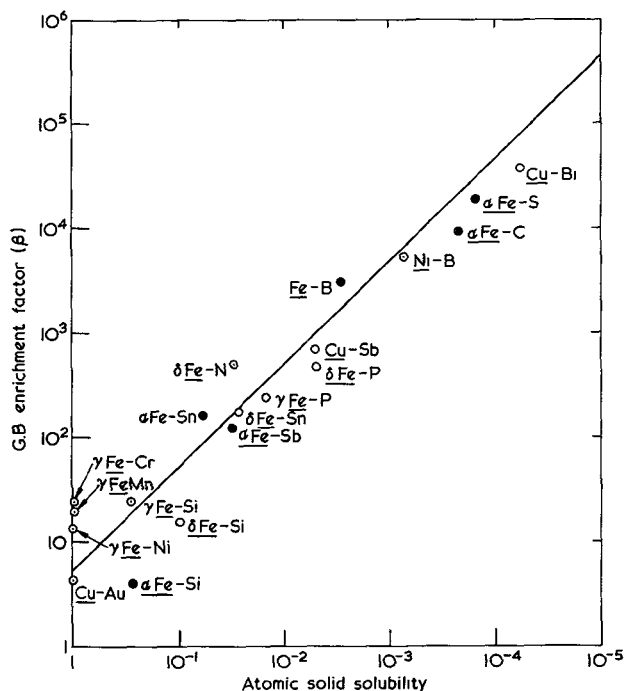


FIG. 19. — Correlation of grain boundary enrichment factor with atomic solid solubility at the temperature of the experiment. This includes data obtained by Auger Electron Spectroscopy (filled points) and data obtained by the interface energy approach.

the enrichment factor for a given species at a given temperature if the solubility is known from the equilibrium phase diagram. It has already proved a useful means for evaluating systems which are impracticable to study by present techniques.

6. Description of grain boundary segregation. —

A basic description of the atomistic and electronic processes which give rise to a non-uniform equilibrium redistribution of solute species is closely bound up with alloy theory, which will not be considered here. The subject has also been presented less rigorously in terms of elasticity theory, by computing the elastic distortional energy produced in fitting a large solute atom in the form of a hard sphere, into a smaller lattice hole. The elastic strain energy thus calculated, using the equations derived by Pines [35] and other authors, measures the energy with which the solute is rejected from the lattice. On the other hand, the energy of segregation (like the free energy of adsorption) is a differential term, here the difference between the free energies of the solute atom in a lattice site and in a grain boundary site. Earlier calculations using the Pines model assumed that the solute atom was totally relaxed in the grain boundary site which is probably a crude simplification. Another problem in this procedure is to know the effective atomic size of an atom present as a solute in the matrix, and because the difference in atomic size between solvent and solute enters the calculation as a square law, any error is magnified. In passing however, we

notice that the computed elastic misfit energies for one group of systems is 15.5 kcal per mole (P in δ -Fe) ; 16.4 kcal per mole (P in γ -Fe) ; 25.2 kcal per mole (Sb in Cu) and 31.9 kcal per mole (Bi in Cu) as determined earlier by Hondros [21]. Compared with corresponding values of the enrichment factors from figure 19, which should reflect the energy of segregation, there is a surprising agreement in the order of increasing surface activity although not at a quantitative level. Since solid solubility includes quantities such as atomic misfit as well as a valency effects, the best pragmatic guide to grain boundary enrichment tendency is the correlation in figure 19, rather than elastic strain energy calculations.

Computations of the type carried out by Guyot [36] are probably the next most fruitful stage of theoretical development of this subject — here the bonding between the atoms is expressed by a known inter-atomic force law and the energy changes involved in bringing a solute atom to a defined site in the neighbourhood of a grain boundary of known simple geometry is computed.

At the present time and in keeping with the ideas of the Introduction, a more macroscopic model of grain boundary segregation is probably more useful. This has the advantage of averaging out differences in specific behaviour between different grain boundaries and also variations in binding energies of solute atoms to various types of grain boundary site. Using a regular solution model, a number of authors, for example, Suzuki [37] have treated the thermodynamics of solute segregation to stacking faults, and McLean [3] derived a similar equation for segregation to grain boundaries, of the form,

$$\Gamma_b = \frac{X \exp \frac{Q}{RT}}{1 + X \exp \frac{Q}{RT}}$$

where the grain boundary concentration is expressed in terms of the proportion of available sites occupied by the segregant ; X is the bulk solute concentration, and Q refers to the energy of segregation. This is formally analogous to the Langmuir isotherm for free surface adsorption, which involves a saturation adsorption, in this case corresponding to a single monatomic layer of adsorbate. In the case of the grain boundary isotherm above, the saturation level would correspond to the occupation of the available sites in an idealised grain boundary model, that is, somewhat less than half a monatomic layer.

The experimental demonstration of multiple layer equilibrium segregation in iron-tin alloys led Seah and Hondros [9] to treat the data according to multi-layer adsorption theory, by use of a grain boundary analogue of surface adsorption. In this treatment, the BET theory [38] was shown analyti-

cally to fit the experimental results better than any other multi-layer adsorption theory. The original BET theory is of the form,

$$\frac{v_m}{v} \frac{p}{p_0 - p} = \frac{1}{K} + \frac{K - 1}{K} \frac{p}{p_0}$$

where v_m is the quantity that will cover the surface with one monolayer (for the grain boundary analogue, the symbol is X_{b_0}) ; v is the quantity adsorbed at pressure p (here the analogues are X_b and X_c) ; p_0 is the pressure at which the gas condenses (here taken as X_{c_0} , the maximum bulk solubility beyond which the solute precipitates) ; K has the form $\exp E/RT$, and $E = E_1 - E_L$ where E_1 is the heat of adsorption of the first layer and E_L that of all subsequent layers, and corresponds to the heat of liquefaction of the gas.

Thus the grain boundary analogue for multi-layer segregation takes the form

$$\frac{X_{b_0}}{X_b} \frac{X_c}{X_{c_0} - X_c} = \frac{1}{K} + \frac{K - 1}{K} \frac{X_c}{X_{c_0}}$$

In segregation situations where several monatomic layers of segregate can build up at the grain boundary, the above isotherm describes the behaviour. This generalised treatment of grain boundary segregation also allows for the situation where there is a fixed number of grain boundary adsorption sites, and in this case, a form of the equation can be derived which approximates to the McLean adsorption equation given above. In fact, it was observed that segregation of sulphur in iron corresponds to this latter isotherm, which parallels a chemisorption process with a high heat of adsorption.

From the above, grain boundary segregation can be considered phenomenologically as an extension of free surface adsorption theory. In a detailed study of segregating systems, it is normally difficult to anticipate the appropriate isotherm. At this juncture, it is felt that systems that have high surface activity (such as sulphur in iron and oxygen in iron) which chemisorb onto free surfaces, behave according to the McLean (Langmuir) model. Again, tin in iron and possibly antimony and arsenic in iron reflect a grain boundary *physisorption* behaviour and can give rise to multiple layer segregation according to the BET model.

Since a detailed study of segregation in a given system requires a knowledge of the relevant adsorption isotherm, the future might see the experimental determination of segregation isotherms for important systems analysed by procedures mentioned above, in a phase of scientific activity to parallel the experimental determination of a large number of adsorption isotherms by surface chemists in the past.

7. Multiple segregation at grain boundaries. — Most of the data represented in figure 19 was obtained on binary systems, and the correlation refers strictly to binary systems. Thus when used in a predictive way on multi-component systems, this plot may be approximate if there should exist co-operative or competitive segregation among the various solute species.

The direct quantitative study of mixed segregation behaviour in multicomponent systems has not been pursued thoroughly. There is however some information obtained indirectly from past metallurgical observations on the effects of adding a known component in an embrittling system. Such observed changes may or may not reflect segregation interactions — the changed mechanical properties may arise from other causes, for example, the kinetics of segregation may be affected, or the third component may result in lattice softening, thereby throwing less stress onto the grain boundaries. One of the most well established effects is that of carbon, which undoubtedly militates against the phosphorus embrittlement of iron [39] and the tin embrittlement of iron [40]. There are many metallurgical observations of this nature that can be cited, as for example, the improvement in the bismuth embrittlement of copper produced by additions of lithium [41]. It should however be noted that many of these earlier observations are contradictory and it is difficult to arrive at an acceptable consensus of views on the effects of particular trace impurities in multi-component systems, especially in ferrous alloys. This is probably due to the fact that deliberate variations in the content of a given impurity led simultaneously to changes in the levels of other unknown impurities during the alloy preparation stages.

These metallurgical studies are valuable both from the practical point of view and also in that they suggest that grain boundary segregation interactions or exchange reactions at grain boundaries may be possible. A more recent comprehensive study of this type was carried out by Jolly and Goux [42] who showed that sulphur has a marked embrittling effect on very high purity iron, an effect which can be easily masked by the presence of carbon and other elements at very dilute levels. This marked sensitivity of iron to the presence of low quantities of sulphur is illustrated in figure 20, from the work of these authors. The ductile/brittle transition temperature alters rapidly with increasing sulphur content and low levels of carbon up to 50 ppm are effective in reducing this sulphur-induced embrittlement.

We note that the observation of high sulphur sensitivity is consistent with figure 19 which predicts a very high sulphur enrichment factor, occurring at the top right hand corner of the plot. To indicate the confusion in this type of observation,

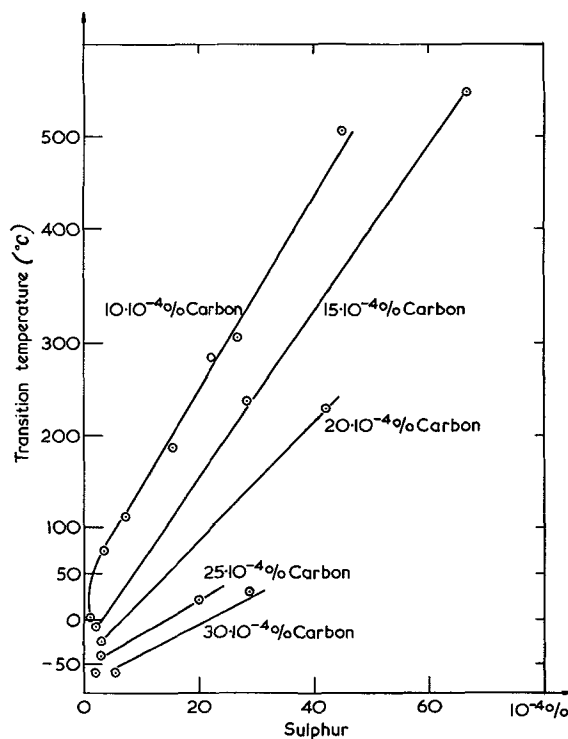


FIG. 20. — The effect of increasing carbon content on reducing the sulphur embrittlement of iron, as reflected in a lowering of the ductile/brittle transition temperature (Ref. [42]).

contrary to earlier views, Jolly and Goux did not observe a specific embrittling effect of oxygen, claiming that earlier observations were probably due to undetected sulphur. Furthermore, it was suggested by these authors, in common with previous notions, that the beneficial effect of carbon is due to an improvement in grain boundary cohesion produced by the competitive exchange of sulphur by carbon at the boundary. There is no clear evidence that the mechanism for the beneficial effect is this exchange reaction at the boundary. Another possibility is that there may be metastable carbon-sulphur interactions in the bulk, thereby reducing the sulphur activity of the bulk. For higher carbon contents, another possible indirect mechanism for an improvement effect of carbon is that a greater fraction of carbide phase is formed, and if the detrimental species segregates well to the carbide-ferrite interfaces, there may be a net diminution in the bulk activity of the detrimental species.

There exist very few direct studies of competitive segregation and these have been made in recent years using Auger Electron Spectroscopy. Thus in the system Fe-Sn-S, Seah and Hondros [9] show that grain boundary tin enrichment levels were not affected by sulphur segregation: the effects appeared to be cumulative, whereas, in a later study, Seah and Lea [43] observed that for the free surfaces of these alloys, there is a strong competitive reaction between these species for adsorption

sites on surfaces. Thus, although it is difficult to generalise at this stage, the evidence so far suggests that active species, such as tin, phosphorus and sulphur segregate in iron cumulatively in the first approximation, and their effect on grain boundary cohesion can also be considered as cumulative.

In the case of alloying elements such as chromium and nickel in steel, there may exist on the other hand, strong interactive segregation effects with highly surface active elements. It is worth noting that in earlier metallurgical studies, Steven and Balajiva [44] and also Low *et al.* [45] demonstrated in a series of experiments that temper embrittlement in steels requires the co-operative effects of a residual surface active element and alloying elements such as chromium and nickel. This was later confirmed directly using Auger Electron Spectroscopy by Joshi and Stein [10], who showed that nickel and chromium do not segregate in the absence of antimony in steel, and in fact segregation of these elements occurs only in the presence of active species such as antimony, tin and phosphorus. This is illustrated, from the results of these authors, in figure 21 which shows that the

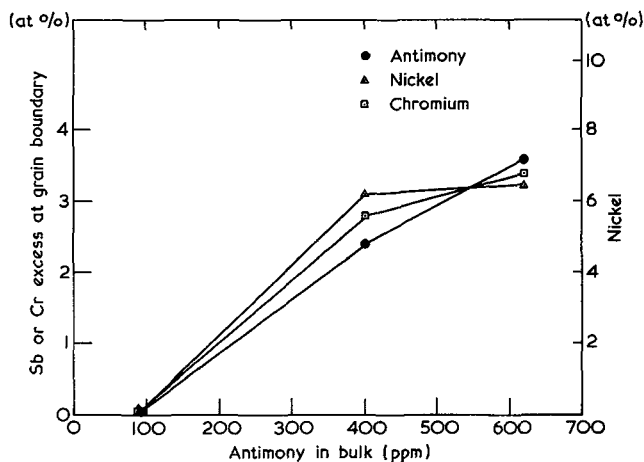


FIG. 21. — Grain boundary excess of Sb, Ni and Cr in iron and its dependence on bulk Sb content (Ref. [10]).

amount of chromium or nickel excess at the boundaries increases with increasing bulk antimony content. Clearly, such results indicate a positive segregation interaction between nickel, chromium and other surface active agents.

8. Segregation depletion of bulk solutes. In a discussion of segregation behaviour, it is normally assumed that the solute levels constitute an inexhaustible reservoir so that segregation at grain boundaries does not affect the bulk solute concentration. In systems where the surface active element is at a very dilute level, and if the grain size is very small, the amount of solute fixed at the grain boundaries may be comparable with the normal bulk content. The regimes of microstructure,

composition and surface activity in which this may occur are worth discussing.

Consider first a system in which the bulk chemical potential of a surface active species is automatically adjusted by contact with the environment or some other reservoir. Thus, for example, nitrogen in α -iron has a high surface activity and also a low equilibrium bulk solubility. Figure 22 gives a comparison of the total nitrogen locked at grain boundary sites for grain sizes of $1\ \mu$ and $10\ \mu$, and that in solid solution at equilibrium with 1 atmosphere of nitrogen [4]. Thus, for iron with a large grain size (greater than $10\ \mu$) the bulk of nitrogen contained in the iron is held in solid solution; the proportion locked at grain boundaries increases as the grain size decreases and at $1\ \mu$ grain size and at about $650\ ^\circ\text{C}$, there is as much nitrogen in the grain boundaries as there is in the lattice. This illustrates that in experimental measurements of the sorption of gases in metals, there should be a full awareness of the specific high absorptivity of grain boundaries and accordingly, material with large grain size should be used. Conversely, an experimental determination of the variation of gas content with grain size can give a direct measure of the amount of gas adsorbed to grain boundaries. This could be a useful experimental technique in systems which are difficult to study directly such as by Auger Electron Spectroscopy.

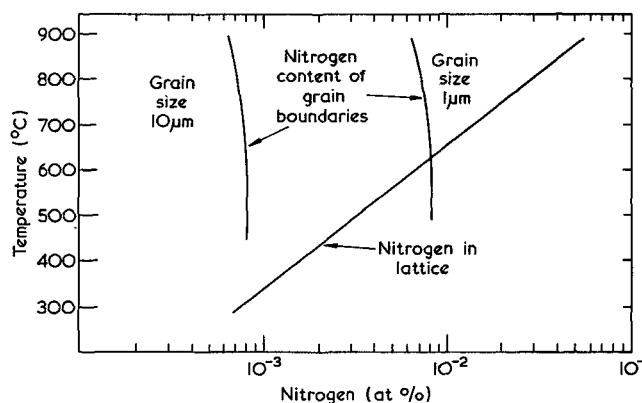


FIG. 22. — A comparison of nitrogen locked at grain boundaries with that in solid solution in iron, at equilibrium (Ref. [4]).

In metal alloy systems which display high surface activity, such as bismuth in copper, where the maximum solid solubility of the bismuth is about 0.02%, there could result appreciable changes in bulk composition following segregation to interfaces. The behaviour for this system is shown in figure 23, which was computed for an idealised array of polyhedral grains of equal cell size. Assuming that one monatomic layer forms at the grain boundaries, the 0.005% bismuth alloy will suffer depletion at a grain size of $100\ \mu$ and severe depletion at grain sizes less than $30\ \mu$. Because the actual grain boundary segregation level depends on

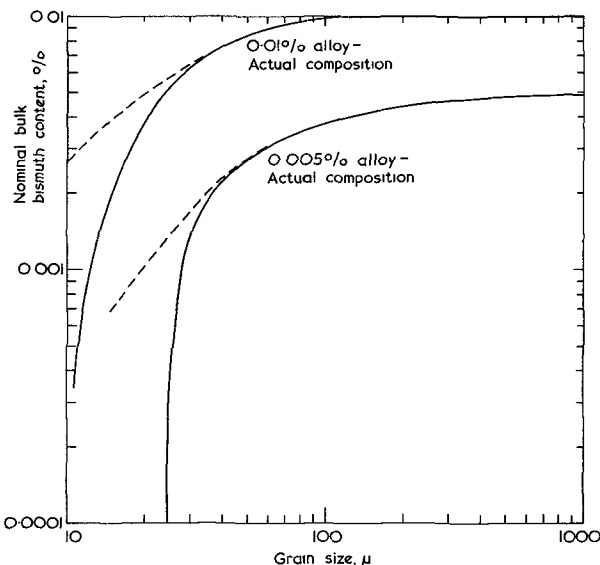


FIG. 23. — Effect of grain size on nominal bulk Bi composition in Cu-Bi alloys in the presence of segregation (assumed one monatomic layer).

the instantaneous equilibrium bulk composition, the assumption of a constant monolayer at the grain boundaries may be a severe requirement for the dilute level; in practice, there will be a self-regulating mechanism which will not permit the bulk concentration to be reduced to zero as suggested in the figure and these calculated curves should diverge in the manner shown by the broken lines at the lower concentration end of the scale.

Thus considering the above as an archetypal system for high surface activity and low solid solubility (less than 0.01%), as a general rule, for a grain size of above $100\ \mu$ the effects of segregation on bulk levels will be negligible.

An interesting corollary of the above, of relevance to means of avoiding segregation embrittlement, is that for a given bulk concentration at this dilute level, the finer the grain size the more of the harmful residual that can be scavenged from solid solution and spread out along the grain boundary surfaces. For a very small grain size, the amount of segregant per unit of grain boundary surface could thus reach below the critical embrittlement level (say, about 0.5 monolayer).

8.1 PHASE BOUNDARIES AND SEGREGATION. —

The important interface between ferrite and cementite has a measured free energy which is comparable to the average grain boundary energy in α -iron [46]. This suggests that in the first approximation, this interface is as structurally incoherent as a high angle grain boundary and hence, one would expect it to play a segregating role in steels. There is, for example, the observation of Restaino and McMahon [47] that in the presence of antimony, the ferrite/cementite interface loses its normal high tenacity and examples were noted of

debonding at these interfaces. Unfortunately, there are not any direct measurements of segregation to phase boundaries, and this highlights an important experimental need for future research activity.

It was indicated earlier that carbon has a beneficial effect on the embrittlement of iron by tin, sulphur and phosphorus. It would be interesting to examine the possibility that the beneficial effect is due to the depletion of the harmful element from the bulk by adsorption to the cementite-ferrite interfaces and consequently the reduction of the equilibrium grain boundary level. In short, can phase interfaces act so as to deplete the bulk of a harmful surface active element?

An accurate assessment of this depends on the carbon content in question, the form of the pearlite, whether it is lamellar, spheroidal and other morphological features such as size and distribution of spheroids. Consider for the purposes of a crude assessment, an idealised cube of fully pearlitic structure, with the flat continuous platelets parallel to one side, and with the alternating phases being equidistant and having a width of $1\ \mu$. A half monolayer coverage of phosphorus on all these interfaces would be equivalent to a bulk phosphorus content of 0.01%; for tin, it would be 0.014%. Since the phosphorus and tin embrittling contents are at this general level (depending upon prior heat treatment), it may be worth considering the possibility of reducing the phosphorus and tin contents to below criticality by this approach.

9. Non equilibrium segregation. — During the past decade, certain grain boundary phenomena have been noted which are sensitive to the rate of cooling from a high temperature and also which are believed to be due to kinetic processes. This was heralded by a remarkable series of experimental observations by Westbrook and his collaborators (reviewed earlier in ref. 5), which concern the significant changes in microhardness indentation values at the grain boundary region compared with the bulk, in certain dilute alloys. With careful experimental handling techniques the effects were observed to be reproducible. A typical set of results is shown in figure 24, which also illustrates that both hardening and softening in the grain boundary regions may be induced, and that the effect is sensitively dependent on the nature of the alloying species at the dilute level [48]. A large number of systems, both alloys and intermetallics were studied and the microhardness phenomenon was established in these also. The detection of microhardness changes is very sensitive to instrumental parameters and a number of other research workers failed to reproduce these results. However, in the University of Sheffield, Braunovic, Haworth and collaborators succeeded in demonstrating this independently in iron alloys and figure 25, from their

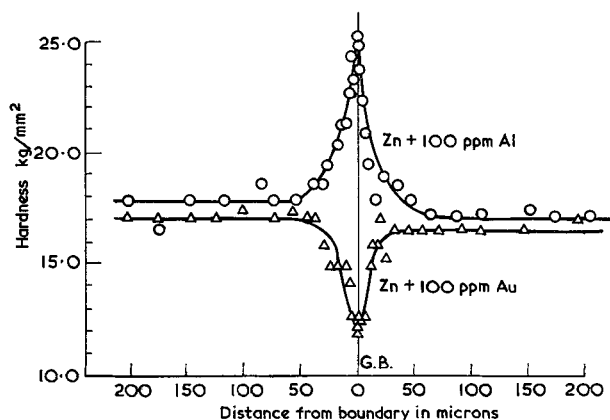


FIG. 24. — Microindentation hardness profiles across grain boundaries in Zn showing both a *hardening* and a *softening* effect (Ref. [48]).

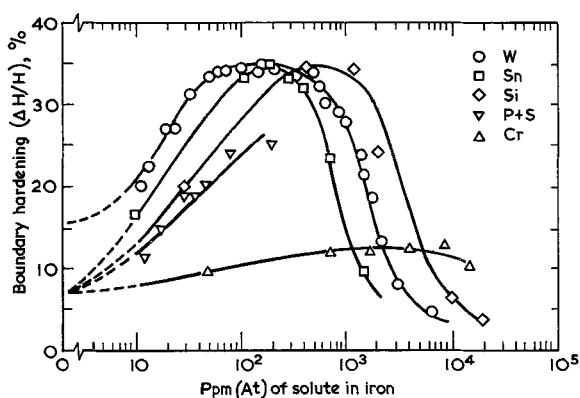


FIG. 25. — Effect of a number of additives at a dilute level on the grain boundary hardening parameter (Ref. [49]).

work, shows typically an effect of a number of additives at dilute level [49]. In addition, a close study of the phenomenon by these authors [50] in terms of the elastic recovery of the hardness impression and other aspects of the micro-indentation technique proved reasonably that the increased hardness was not a characteristic of the testing technique but was apparently associated with a narrow band of material about the grain boundary that had different elastic properties.

Examination of the numerous systems that have now been documented and which display this grain boundary hardening phenomenon shows that there is no clear correlation between solute species which induce the grain boundary hardening and surface active species which we have examined earlier and which lead to equilibrium segregation. Another important feature of this phenomenon, as shown in figure 24, is that the effect extends to distances of the order of microns beyond the grain boundary and such a gross effect can hardly be accounted for by the monolayer levels of segregation that were considered above.

For these important reasons at least, it is right to distinguish this phenomenon from the equilibrium segregation that we have been concerned with. In addition, the origin of this effect must be different from that of equilibrium segregation and the mechanism that appears to satisfy most observations is that first suggested by Seybolt, Westbrook and Turnbull [51], and amplified and generalised later by a number of associated authors, for example, Anthony [52], namely, the *vacancy drag* model. Here it is supposed that during a temperature change, vacancies flow to grain boundaries so as to preserve their thermal equilibrium value and because of the associated transport of solute-vacancy pairs, a solute concentration can be set up about the grain boundary which acts as a sink. The strength of the effect depends upon the interaction energy between the solute and the vacancy. The analysis of Anthony and other authors showed that this effect may set up solute concentrations over distances that compare with the grain boundary hardness profiles (that is, of micron dimensions) and it is consistent with other observations such as the effect of quench rate.

We note however that there is yet no direct measurement of solute concentrations profiles at grain boundaries in the manner of figures 9 and 10 for equilibrium segregation, and furthermore their correlation with enhanced grain boundary hardening. In view of the current availability of suitable analytical techniques, for example, transmission electron microscopy with energy analysis, this is an unnecessary deficiency in the present state of this subject and work directed to the measurement of these profiles will surely advance it.

Metallurgically, such non-equilibrium segregation effects at grain boundaries could be quite important. Thus quite recently, Williams, Stoneham and Harries [53] observed by an optical microscope autoradiographic technique that boron segregates to grain boundaries in type 316 Austenitic steel, following cooling at 50 °C per second. Furthermore, the extent of the segregation diminished with increasing solution treatment temperature, in a manner contrary to equilibrium segregation behaviour and they interpreted their results in terms of the solute-vacancy flux mechanism. The subject has also close affinities with a form of segregation at phase interfaces which is considered to occur during the growth of a new phase. Here, because of differences in kinetics, a solute partitioning may occur, leading to the piling up of various species at the phase interfaces, the height and width of the pile-up depending on kinetic considerations, as first suggested by Bruggeman and Kula [54] as a possible explanation of temper brittleness and later extended by Rellick and McMahon [55] in connection with 350 °C embrittlement. Further work is required to characterise the conditions in which

such non-equilibrium processes, whether of the quench type leading to grain boundary hardening, or the phase-growth type leading to interface solute build-ups may dominate over the equilibrium processes or even co-exist with these processes.

Ultimately the unequivocal distinction will be made in terms of the measured concentration profiles about the interfaces and the thermal conditions which give rise to them.

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DISCUSSION

Ph. MAITREPIERRE : In your review, you mentioned the importance of the state of segregation of the elements (atomic, nuclei of phases, etc.).

Would you comment on the possibilities of gaining new insight into this problem (for instance through use of AES chemical shifts) ?

E. D. HONDROS : This is an interesting point, and experimentally a difficult problem to obtain information on the chemical state of segregating species. Any information obtained from exposed grain boundaries, either by ESCA, or by AES, fine structure appearance, still leaves the question open as to whether this is the situation on a pristine boundary. Similar doubts may exist with FIM Atom Probe studies on surface exposed atoms, although some interesting information is already being obtained by the Cambridge school on the existing of segregate carbon dimers and trimers.

Ultimately, the unequivocal information will have to come from examination of integral boundaries — how this will be done is another matter.

K. LUCKE : You showed a distribution curve for the concentration of Mg in Al across the boundary. The width of this curve was more than 1000 Å. Since it is improbable that the Mg-atoms feel the boundary being many hundreds of atomic distances away ; I would like to ask whether this feature might be caused by some errors of measurements and must not be taken serious, or, if you believe in this curve, how this large width can be explained. Also for the case that this curve could not represent the equilibrium distribution, but would be of kinetic nature, its width cannot be understood. It should only occur that the equilibrium enrichment is not reached because of kinetic effects, but not that it is surpassed. It should also play no role whether the Mg-atoms are in solid solution or precipitated.

E. D. HONDROS : First let me remind you that I used this figure to illustrate the potential of the technique in studying phenomena on integral grain boundaries. These are the results of careful experimentalists and I accept them in good faith — also, similar types of profiles have been obtained in Al-Mg-Zn type systems by other workers. Although I agree entirely with you that this cannot be an equilibrium phenomenon of the type we have been discussing, I see no reason why non-equilibrium profiles of this magnitude would not be built up in the manner envisaged by, for example, Anthony (see ref. 52 of the review).

R. BALLUFFI : The experimental determination of the solute atom distribution normal to the boundary by the method of ion sputtering is complicated by a possible lack of precision in the location of the fractured surface and also by the

redistribution of solute atoms in the target due to the sputtering process itself. Both effects would tend to spread out the distribution, and therefore, the actual solute distribution may have been appreciably narrower than indicated by the data shown.

E. D. HONDROS : On the location of the fracture surface, this is usually carefully checked, and also, similar composition profiles have been determined by Seah at the NPL on fracture surfaces that were oriented in relation to the ion beam and in which the grain size was well above the diameter of the AES electron beam.

Admittedly, same error is possible here. On the second point, while most workers in the field are conscious of the possibility of ion beam/target effects (and work at the NPL has shown that in the study of glasses this is extremely important), in metal/chemisorbed layer systems, it seems that this is not a serious problem in most cases. However, a possibly serious source of error which may affect the profile shapes is the sputter yields that are used in computerizing the distances — these yields are usually those of the individual pure elements rather than of the elements present in the alloys.

I agree that the real profiles are possibly narrower than those shown here.

S. HOFMANN : Is it possible to relate the sputtering profiles of segregated species you have shown to a real concentration profile perpendicular to the boundary, thus giving a figure of the range of the grain boundary-impurity interaction force in terms of the dependence of the interaction potential on the distance from the boundary ?

E. D. HONDROS : Unfortunately, the shapes of the concentration profiles obtained by sputter-erosion/AES procedures are not sufficiently accurate for this otherwise very useful information. Perhaps, analysis obtained by FIM/Atom Probe procedures might yield more accurate data.

P. GUYOT : Did you try to fit your concentration profiles versus the distance from the boundary, as determined by AES, to such an equation :

$$c(r) \propto \exp(Ar^{-n})$$

this, in order to get an experimental idea about the interaction energy between boundary and impurity ?

E. D. HONDROS : Although such an equation may be fitted, it is doubtful, for reasons of experimental accuracy (as mentioned in reply to Balluffi's and Hofmann's questions) whether this would be sufficiently reliable to have any meaning — the only significance of these profiles is that the segregation is very close to the boundary.